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CHARACTERIZATION OF REGENERATED CELLULOSE MEMBRANES HYDROLYZED FROM CELLULOSE ACETATE*

Yun Chen[a,b], Xiao-peng Xiong[b], Guang Yang[b], Li-na Zhang[b**], Sen-lin Lei[a] and Hui Liang[a]

[a] *Electron Microscope Lab of Medical School, Wuhan University, Wuhan 430072, China*

[b] *College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China*

Abstract A series of cellulose acetate membranes were prepared by using formamide as additive, and then were hydrolyzed in 4 wt% aqueous NaOH solution for 8 h to obtain regenerated cellulose membranes. The dependence of degree of substitution, structure, porous properties, solubility and thermal stability on hydrolysis time was studied by chemical titration, Fourier transform infrared spectroscopy, scanning electron microscopy, wide-angle X-ray diffraction, and differential scanning calorimetry, respectively. The results indicated that the pore size of the regenerated cellulose membranes was slightly smaller than that of cellulose acetate membrane, while solvent-resistance, crystallinity and thermostability were significantly improved. This work provides a simple way to prepare the porous cellulose membranes, which not only kept the good pore characteristics of cellulose acetate membranes, but also possessed solvent-resistance, high crystallinity and thermostability. Therefore, the application range of cellulose acetate membranes can be expanded.

Keywords Hydrolysis, Cellulose acetate, Thermal stability, Regenerated cellulose membrane, Pore size, Solvent-resistance, SEM

INTRODUCTION

Membrane separation proceses, an energy saving and high-efficiency technology, have been widely used for separation tasks in the chemical, food and biotechnological industries[1, 2]. Cellulose acetate (CA) as a membrane material has found extensive commercial applications, because of its relatively low cost, high selectivity, high permeability and easiness of controlling pore size. The microporous membranes from CA with dense spongy structure or asymmetric fingerlike morphology can be obtained by adjusting the composites and coagulation condition[3, 4]. Therefore, CA membranes can be used not only in reverse osmosis (RO)[5], but also in the procedure of ultrafiltration (UF)[6], microfiltration (MF)[7], pervaporation (PV)[8] *etc.* In order to develop high-performance materials, blending[9–11] and surface modification[12,13] of the membranes have been intensively studied, such as blends of CA/poly(butylene succinate)[9], CA/chitosan[10] and CA/polyurethane[11], low temperature oxygen plasma modification or irradiation treatment. Moreover, the degree of substitution of CA membranes plays an important role in determining performance[5]. When the degree of substitution (DS) is about 2, CA can easily be dissolved in organic solvents such as acetone, pyridine and dimethyl sulfoxide (DMSO), so that its application in organic solvents system is limited[3].

Regenerated cellulose (RC) has good organic solvent-resistance, high thermal stability and good mechanical properties. Due to the existence of strong inter- and intra-molecular hydrogen bonds in RC molecules, it can only be dissolved in strong polar solutions[14] such as cuoxam, LiCl/*N*,*N*-dimethylacetamide (DMAC), DMSO/polyformaldehyde (PF), and only membranes with spongy structure can be obtained. Hydrolysis of CA

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** Corresponding author: Li-na Zhang (张俐娜), E-mail: lnzhang@public.wh.hb.cn

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membranes is a simple method to obtain RC membranes with various pore sizes.

In this paper, CA membranes were prepare by using formamide as additive, and then hydrolyzed in alkali solution to obtain regenerated cellulose membranes having better organic solvent-resistance and higher thermal stability compared with the raw materials. The effect of hydrolysis time on DS, pore size, pore characteristics, and thermal stability of the membranes was studied.

EXPERIMENTAL

Preparation of Membranes

Cellulose acetate (E-398-3) with DS = 2.45 was obtained from Eastman Corporation. It was dissolved in a mixture of acetone and formamide with vigorous stirring and degassed. The resulted mixture solution was spread over a glass plate at 25℃ to form a layer of 0.25 mm thickness. The plate was immersed in ice water immediately for 1 h, then washed in water and dried in air at room temperature. By changing the ratios of CA, acetone and formamide, *i.e.*, 23:55:22, 20:48:32, 17:41:42, 14:34:52 and 11:27:62, a series of transparent membranes were obtained, and designated by CA1, CA2, CA3, CA4 and CA5, respectively.

CA4 was hydrolyzed in 4 wt% NaOH aqueous solution for the desired time at 25℃, then washed with water and dried in air at room temperature. By changing the hydrolysis time, a series of membranes designated by CA4-n (n-stands for the hydrolysis time, h) were prepared, respectively, *e.g.*, CA4-4, CA4-8, CA4-16 and CA4-24.

Characterization of the Membranes

The DS of hydrolyzed cellulose acetate membranes was determined by the following chemical titration method. A piece of CA membrane was dipped into 20.00 mL 1 mol/L NaOH aqueous solution for the desired time, then the concentration of the solution was measured by neutralization titration with $H_2C_2O_4$. The DS of pre-hydrolyzed CA membrane was calculated from:

$$DS_0 = [162 \times 20\ (c_0 - c_e) / [1000W - 42 \times 20\ (c_0 - c_e)] \quad (1)$$

The DS of post-hydrolyzed CA membrane was calculated as follows:

$$DS_t = DS_0 - [162 \times 20\ (c_0 - c_t)/1000W] \quad (2)$$

where c_0 and c_e are the concentrations of NaOH solution at the beginning time and at the time when CA membrane was totally hydrolyzed, mol/L, c_t is the concentration of NaOH solution at the designated time, mol/L. DS_0 and DS_t represent the DS of pre-hydrolyzed and post-hydrolyzed CA membrane, respectively, and W is the weight of pre-hydrolyzed CA membrane, g. The theoretical DS of E-398-3 was 2.45[3].

Scanning electron micrographs (SEM) were taken on a Hitachi S-570 microscope. The pre-hydrolyzed and post-hydrolyzed membranes were frozen in liquid nitrogen and fractured immediately, and then dried in vacuum, coated with carbon and gold for SEM observation of the surfaces and cross-sections. The electron micrographs were analyzed by a high resolution imaging analysis system (HLPAS-1000) to evaluate the average pore size $2r_e$ by extracting pore parts with monitoring of the difference in brightness[15].

At the meantime, an improved Bruss membrane osmometer, based on the flow rate method reported in our previous work[16], was used for measuring the mean pore radius (r_f) of the wet membranes. The porosity of the membrane was calculated according to the previous method[16], and the r_f value was evaluated by Kuhn's equation[17].

Infrared (IR) spectra were recorded with a Nicolet FT-IR spectrometer (SX-170). The samples were prepared by the KBr-disk method. The X-ray diffraction (XRD) was measured with an X-ray diffractometer (D/MAX-1200, Rigaku Denki., Japan). The XRD patterns with Cu Kα target at 40 kV and 20 mA were recorded in the region of 2θ from 6° to 40°. The total crystallinity and the crystallinity of cellulose II were calculated with a peak separation method by a computer. The thermal decomposition temperatures of the membranes were measured on a DSC-2C differential scanning calorimeter (DSC, Perkin-Elmer, U.S.A.). The head-space over the sample holder was maintained in a flowing pure nitrogen atmosphere with a flux of 40 mL/min. The rate of heating was kept at 10 K/min.

To study the solvent-resistance, the membranes were dipped into different solvents such as water, alcohol, acetone, DMSO and pyridine at 25℃.

RESULTS AND DISCUSSION

Structure of the Membranes

The dependence of DS values on hydrolysis time of the CA membranes is shown in Fig. 1. It indicates that CA membranes can be easily hydrolyzed. After 30 min, the DS decreased to 0.48, and the acetyls were almost completely removed from CA by dilute alkali solution after 8 h. The DS of pre-hydrolyzed membrane calculated by Eq. (1) was 2.44, similar to the theoretical DS (2.45) of the raw material, E-398-3.

The FT-IR spectra of pre-hydrolyzed and post-hydrolyzed CA4 are shown in Fig. 2. CA4 membrane shows a band at 1744 cm^{-1}, which is attributed to the stretching vibration of C=O. The bands at 1244, 1047 and 907 cm^{-1} correspond to the stretching and bending modes of C—O single bond. These bands decrease in intensity or disappear upon hydrolysis, demonstrating the progressive hydrolysis of the acetyl groups. Moreover, the peak intensity of methylene group at 2927 cm^{-1} decreases with increasing hydrolysis time. This indicates that the acetyl in the cellulose acetate is almost completely hydrolyzed to form the regenerated cellulose membrane in dilute alkali solution.

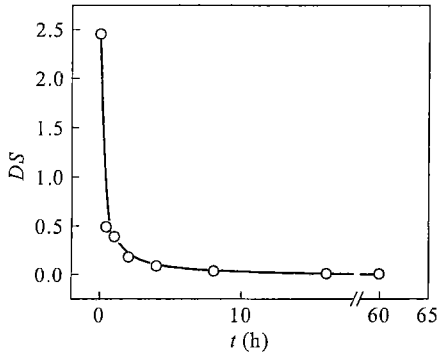

Fig. 1 Dependence of DS of the membranes on hydrolysis time

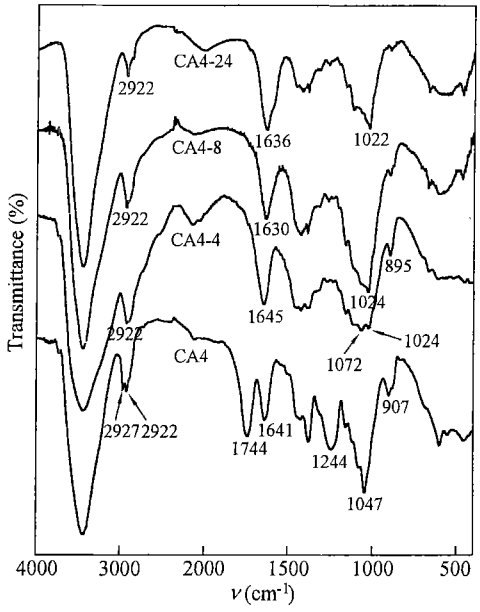

Fig. 2 FT-IR spectra of pre-hydrolyzed and post-hydrolyzed CA4

Figure 3 shows the X-Ray diffraction patterns of pre-hydrolyzed and post-hydrolyzed CA4. It can be recognized that two broad crystal peaks appeared at 2θ = 9.1° and 19.6°. However, after CA4 has been hydrolyzed by alkali, two obvious crystal peaks at 2θ = 12° and 21.7° could appear, which are the diffraction peaks of cellulose II at crystal plane (110), ($1\bar{1}0$) and (200). Total crystallinity χ_C and crystallinity of cellulose II χ_{RC} were calculated by a computer using a peak separation method. The dependence of crystallinities on hydrolysis time is shown in Fig. 4. It indicates that the crystallinities of membranes are clearly improved. When the hydrolysis time was extended to 4 h, both χ_C and χ_{RC} tended to become constant. It can be explained that with the progress of hydrolysis of the acetyl groups, a large number of new hydroxyl groups are produced and lead to the formation of hydrogen bonds. In addition, cellulose molecules in alkali aqueous solution are rearranged, and become denser and more regular, resulting in an improvement of crystallinities, especially that of cellulose II.

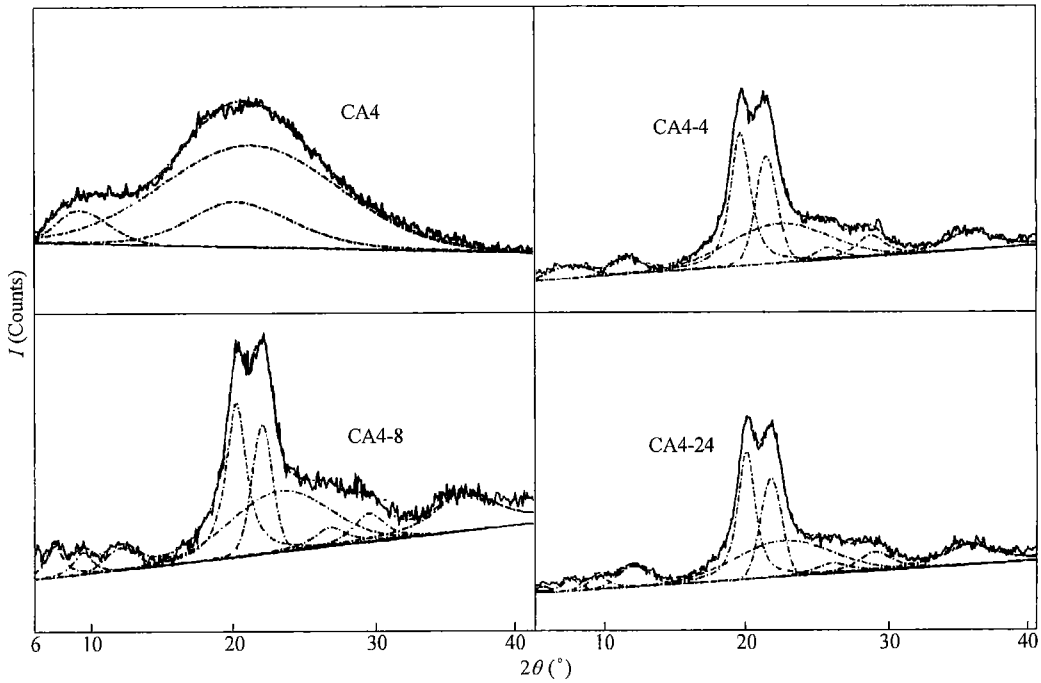

Fig. 3 X-Ray diffraction patterns of pre-hydrolyzed and post-hydrolyzed CA4

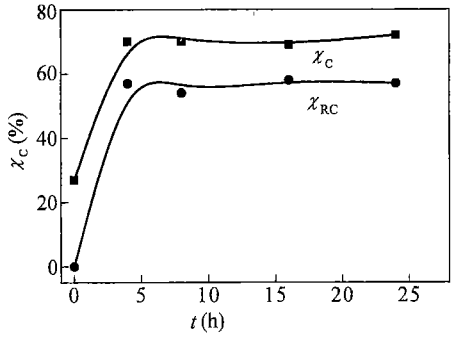

Fig. 4 Dependence of crystallinities of hydrolyzed membranes on hydrolysis time; χ_C — total crystallinity, χ_{RC} — crystallinity of cellulose II

Pore Size of the Membranes

The SEM photographs of the cross-section of the CA membranes and their corresponding RC membranes are shown in Fig. 5. The mean apparent pore sizes $2r_e$ calculated by computer and the mean pore sizes $2r_f$ and porosity P_r evaluated according to the flow rate method are listed in Table 1. These data indicate that the cross-section of the CA membranes has quite uniform pore structure. The pore sizes $2r_e$ and $2r_f$ increase with increasing formamide content (w_{FM}). The pore structure of CA membrane generally depends on two factors: (1) the content of CA in the dope solution, (2) the difference between the rate of water penetrating into membrane and the rate of solvent bleeding from the membrane. The latter influences the route of gelation for membrane casting solution. The diffusion rate of water into the casting membrane was enhanced with the incorporation of formamide into the casting solution; thereby the amount of polymer network formed and the size of large micelle aggregates were increased[18]. The increase of the formamide content improved the pore size due to the faster rate of gelation[19].

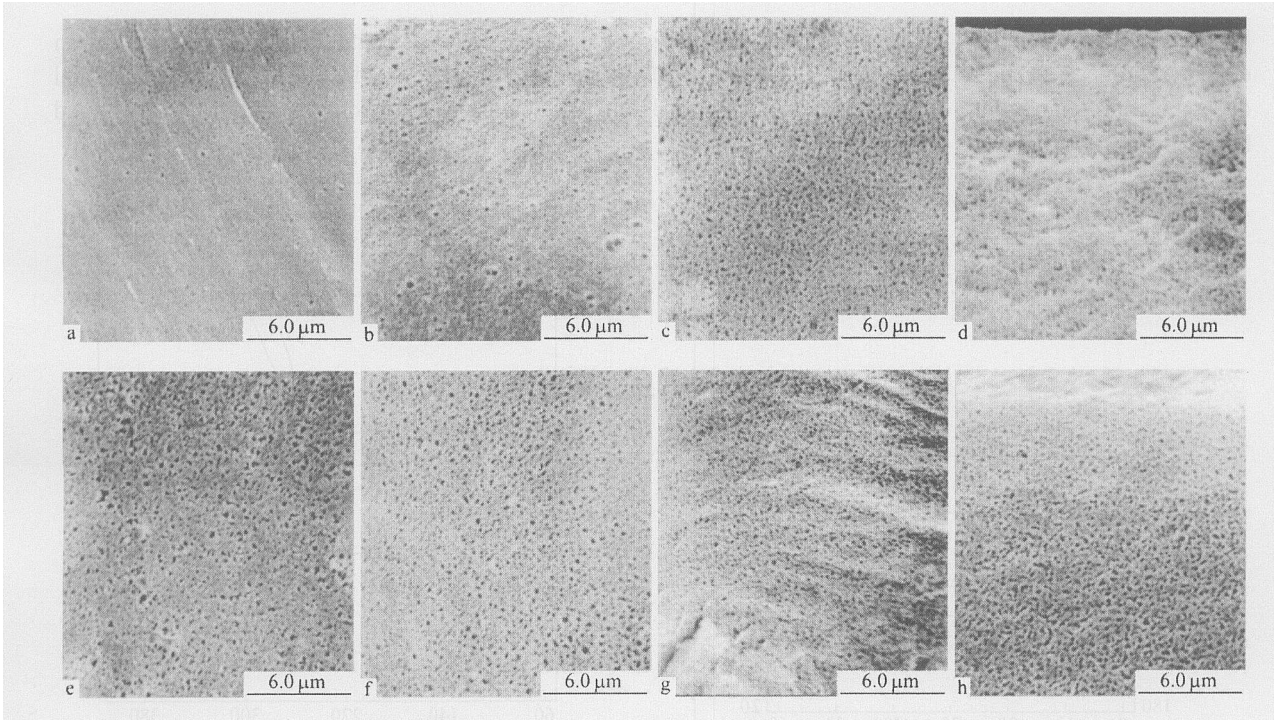

Fig. 5 SEM micrographs of cross-section for pre-hydrolyzed and post-hydrolyzed cellulose acetate membranes
a) CA1; b) CA2; c) CA3; d) CA4; e) CA5; f) CA4-2; g) CA4-8; h) CA4-24

Table 1. Mean apparent pore size $2r_e$, mean pore sizes $2r_f$ and porosity P_r of the CA membranes

Membrane sample	$2r_e$ (nm)*	P_r (%)**	$2r_f$ (nm)**
CA1	84.3	0.47	10.7
CA2	188	0.54	17.9
CA3	216	0.66	23.8
CA4	241	0.74	42.8
CA5	269	0.80	47.5

* Measured by SEM imaging analysis system; ** Measured by osmometry

Figure 6 shows the dependence of pore sizes of CA4 and its hydrolyzed membranes CA4-n on hydrolysis time. The pore size of RC membranes hydrolyzed from CA membrane is slightly smaller than that of the latter but still has the same uniformity as the CA membranes. The pore size of RC membranes decreases with the increase of hydrolysis time. It reaches a plateau when the hydrolysis time is extended to more than 10 h. This implies that cellulose molecules can rearrange and shrink during the process of hydrolysis in dilute alkali solution and reach equilibrium at longer hydrolysis time. The changes of $2r_e$ and $2r_f$ have the same tendency, but the values of $2r_e$ are 6–10 times larger than those of $2r_f$. The $2r_e$ reflects the apparent pore size of the membrane, while $2r_f$ is the effective pore size in the penetration process of the membrane, which is decided by the distribution and shape (closed pores, half-closed pores and straight pores) of the micropores within the cross-section of the membrane.

Thermal Properties of Membranes

The DSC thermograms for pre-hydrolyzed and post-hydrolyzed CA4 are shown in Fig. 7. The melting temperature of CA4 is 278℃. A broad endothermic peak appeared at 264–287℃ after CA was hydrolyzed for 8 h. It can be explained that after membrane was hydrolyzed, some of the hydroxyls became hydrogen bonded and the crystallinity of the membrane increased, leading to an improvement in the thermostability of the membranes and the appearance of an endothermic peak at 287℃. But at the same time, the other hydroxyls in

hydrolyzed chains were not hydrogen bonded, resulting in a decrease of crystallinity and the appearance of an endothermic peak at 264℃ as shown in CA4-8. When CA4 was further hydrolyzed for 16 or 24 h, the thermal decomposition temperature of the membranes rose to 312–313℃ owing to the strong hydrogen bonds formed between the RC molecules.

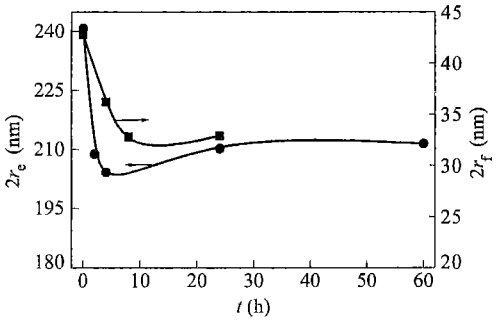

Fig. 6 Dependence of the porous sizes of pre-hydrolyzed and post-hydrolyzed CA4 on hydrolysis time by dilute alkali
● Measured by SEM imaging analysis system
■ Measured by osmometry

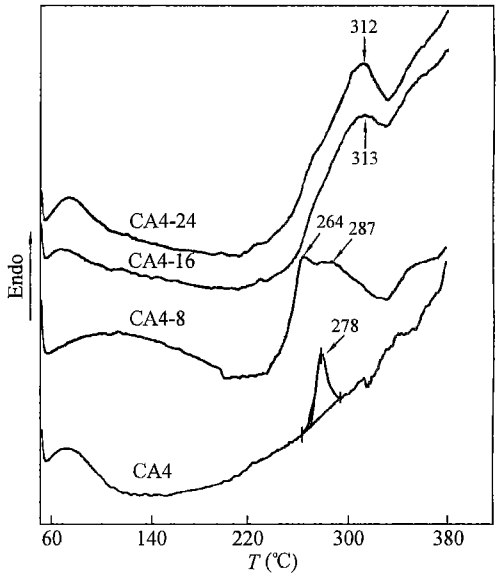

Fig. 7 DSC spectra of pre-hydrolyzed and post-hydrolyzed membranes

Solvent-Resistance of the Membranes

Table 2 shows the solubility of the membranes in different solvents. The pre-hydrolyzed membranes could not be dissolved in water and alcohol, but still could be dissolved in acetone, DMSO and pyridine. However, the post-hydrolyzed membranes become insoluble in the solvents mentioned above, indicating that the solvent-resistance of the membranes is significantly enhanced. Particularly, the RC membranes (completely hydrolyzed CA membranes) have perfect solvent-resistance as well as high crystallinity and good thermal stability, and are also stable in dilute alkali solution, owing to the dense arrangement of the molecules.

Table 2. Solubility of the CA membranes and CA-n membranes*

Membrane sample	Water	Alcohol	Acetone	DMSO	Pyridine
CA5	×	×	O	O	O
CA4	×	×	O	O	O
CA3	×	×	O	O	O
CA2	×	×	O	O	O
CA1	×	×	O	O	O
CA4-1	×	×	×	×	×
CA4-2	×	×	×	×	×
CA4-4	×	×	×	×	×
CA4-8	×	×	×	×	×
CA4-16	×	×	×	×	×
CA4-60	×	×	×	×	×

* × Insoluble; O Soluble

CONCLUSION

A series of cellulose acetate membranes with different pore sizes were successfully prepared with formamide as additive in acetone solvent. The pore size of the membrane increases with increasing content of formamide. The cellulose acetate membranes were hydrolyzed to prepare regenerated cellulose membranes. The degree of substitution of the post-hydrolyzed membranes obviously decreases with an increase of hydrolysis time. After 8 h, almost all of the acetyl groups in the membrane were hydrolyzed off with the formation of regenerated cellulose membranes. The pore sizes of the post-hydrolyzed membranes were slightly reduced but still retain their uniformity. The regenerated cellulose membranes so obtained have better solvent-resistance, satisfactory pore properties, higher crystallinity and good thermostability, compared with the cellulose acetate membranes.

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